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THE EFFECT OF CONDENSED PHASE  
COMBUSTION PRODUCTS ON  
BALLISTIC PERFORMANCE

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FEBRUARY 1992

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U.S. ARMY LABORATORY COMMAND

BALLISTIC RESEARCH LABORATORY  
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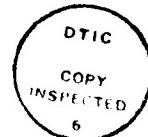
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## 1. INTRODUCTION

The performance of a gun for a given propellant formulation can be estimated by a constant chamber pressure calculation. This calculation assumes that the propellant burns at a rate that produces a constant pressure in the chamber as the projectile moves down the gun tube. The pressure chosen is the maximum pressure that a given gun can withstand. When the propellant is completely consumed, adiabatic expansion takes place as the projectile moves down-bore to the muzzle. These two expansions, one at constant pressure and one adiabatic, determine the gun performance. Although in practice, the constant pressure may be difficult to achieve, this part of the calculation is useful in comparing different propellant formulations. As will be seen later in this report, the adiabatic expansion is virtually the same for all conventional propellants because it depends only on  $\gamma$  (the specific heat ratio), which hardly varies from one propellant to another, and on volume change, which is determined solely by the gun's geometry.

Propellants do differ markedly, however, in their capabilities for producing a specified chamber pressure with the least amount of propellant.

A useful figure of merit for comparing propellant formulations is the impetus, or specific energy, defined by  $RTw/(WM)$ , where  $R$  is the gas constant,  $T$  the temperature, and  $w$  is the mass of gas of molecular weight  $M$ , produced by propellant of mass  $W$  (Freedman 1982). Conventional propellants produce little or no condensed (solid or liquid) phases; so for them,  $w = W$ , and impetus is just  $RT/M$ . For example, using an ideal gas equation of state for the combustion products,

$$P/p = RT/M.$$

From this, the pressure in the chamber can be found for a given loading density,  $p$ . Thermodynamic calculations will determine a flame temperature,  $T$ , and molecular weight  $M$  for a given propellant formulation. (For actual gun conditions, a real gas equation of state must be used.)

Currently, a variety of new energetic formulations are being tested for the electrothermal gun to obtain working fluids with properties that are advantageous for this propulsion concept.

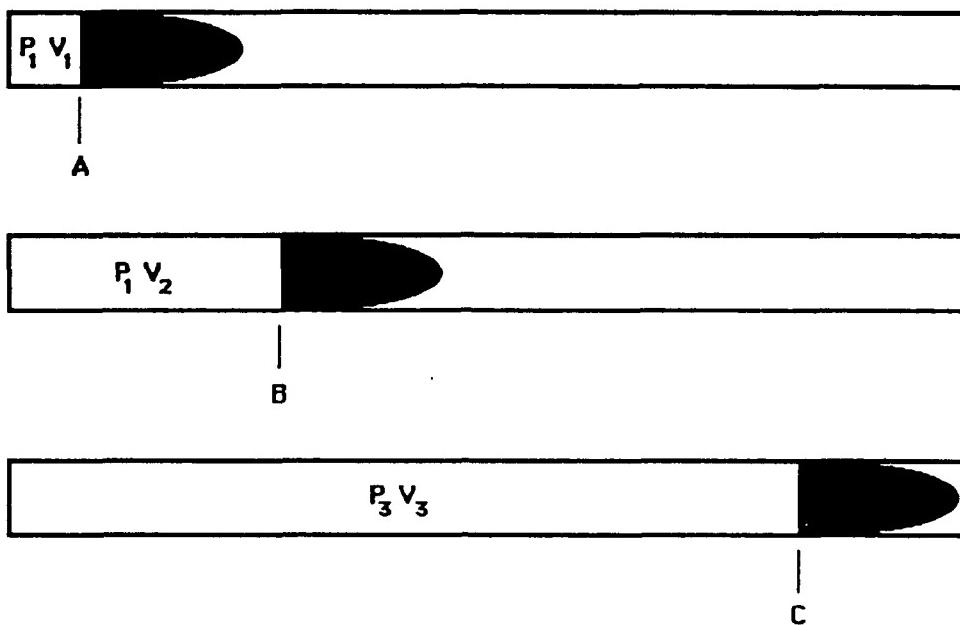
Several of these formulations involve the production of large quantities of solid products. The purpose of this paper is to describe the effect of these condensed phase products on predicted ballistic performance. As can be seen from the calculation of the impetus, products containing large amounts of solids will affect the impetus. As will be seen later,  $\gamma$  is also affected.

## 2. PHYSICAL INTERPRETATION OF $\gamma$

One of the important thermochemical parameters used in interior ballistic calculations is the specific heat ratio,  $\gamma$ . It is defined as the ratio of the heat capacities  $C_p/C_v$ , where  $C_p = \Delta Q/\Delta T|_p$ , and  $C_v = \Delta Q/\Delta T|_v$ . For monatomic gases, this ratio is 1.67; for typical propellant gases, this value is between 1.22 to 1.26. As the molecule becomes more complex and has more internal degrees of freedom,  $\gamma$  approaches 1. The physical reason for this behavior is discussed in the following paragraphs.

The heat capacities measure the energy required to raise the temperature an amount,  $\Delta T$ .  $C_p$  is determined under conditions of constant pressure. Thus, more energy  $\Delta Q$  is required to raise the temperature  $\Delta T$  than in the constant volume case  $C_v$ , since work must be determined in expanding the volume  $P\Delta V$  to maintain a constant pressure. Since  $C_v$  is performed at constant volume, no additional work is involved. Thus, the ratio  $C_p/C_v$  is greater than one.

As molecules become more complex, the number of internal degrees of freedom (df's), (e.g., vibrational and intramolecular rotational modes) increases. Since these internal df's are in equilibrium with the translational df's, part of the energy  $\Delta Q$  must be used in exciting these df's. Thus, for complex molecules, a greater amount of energy  $\Delta Q$  is required for a given change in temperature in both  $C_p$  and  $C_v$ . The amount of energy needed for the work  $P\Delta V$  becomes a smaller percentage of the total  $\Delta Q$  and, hence, the ratio  $C_p/C_v$  approaches 1. Thus, simple products such as atoms have large values for  $\gamma$ , whereas complex products, especially solids, have  $\gamma$ 's approaching 1.



**Figure 1. Schematic of Ballistic Process.**

### 3. CONSTANT PRESSURE CALCULATIONS

To illustrate the effect that  $\gamma$  has on the various portions of the interior ballistic cycle, consider a constant chamber pressure calculation diagrammed in Figure 1. The constant pressure portion  $A$  to  $B$  is maintained while the propellant burns. After the propellant has been consumed, the adiabatic expansion process occurs as the projectile moves down-bore from  $B$  to  $C$ .

For purposes of this discussion, the projectile mass is assumed to be considerably larger than the propellant mass. Hence, the chamber and projectile base pressures are nearly the same. In addition, an ideal gas is assumed, and heat losses are ignored.

The energy required to pressurize the chamber, with no projectile movement, from ambient pressure up to the operating pressure  $P_1$  is

$$Energy(A) = \frac{P_1 V_1}{\gamma - 1}. \quad (1)$$

The energy required during the constant pressure portion of the ballistic cycle as the projectile moves from *A* to *B* is

$$Energy(A \text{ to } B) = \frac{P_1 V_2}{\gamma - 1} - \frac{P_1 V_1}{\gamma - 1} + \frac{mv_B^2}{2}, \quad (2)$$

where *m* and *v<sub>B</sub>* are the mass and velocity of the projectile at *B*. Next, expressing the projectile kinetic energy as

$$\frac{mv_B^2}{2} = \int_{V_1}^{V_2} P dV = P_1 (V_2 - V_1), \quad (3)$$

substituting into Equation 2 and simplifying, yields

$$Energy(A \text{ to } B) = \frac{\gamma P_1 (V_2 - V_1)}{\gamma - 1}. \quad (4)$$

Thus, during the initial pressurization of the chamber and throughout the constant pressure portion of the ballistic cycle (from *A* to *B*), the energy required to attain and maintain a constant pressure increases as  $\gamma$  approaches 1. This is consistent with the physical interpretation of  $\gamma$ —more energy is required to excite the internal degrees of freedom of the products with the low  $\gamma$ .

Now consider the third stage of the ballistic cycle shown in Figure 1. This portion is the adiabatic expansion of the product gases as the projectile moves to the muzzle from point *B*, where the propellant burns out, to point *C* at the muzzle. The work done on the projectile is given by

$$Energy(B \text{ to } C) = \frac{m[v_c^2 - v_b^2]}{2} \quad (5)$$

$$= \int_{V_1}^{V_2} P dV. \quad (6)$$

For an adiabatic expansion,

$$PV^\gamma = \text{constant}. \quad (7)$$

Substituting into Equation 6 for  $P$ ,

$$\text{Energy}(B \text{ to } C) = \text{constant} \int_{V_2}^{V_3} \frac{dV}{V^\gamma} \quad (8)$$

$$= -(\text{constant}) \frac{V^{1-\gamma}}{\gamma-1} \Big|_{V_2}^{V_3} \quad (9)$$

or substituting the limits and using Equation 7,

$$\text{Energy (B to C)} = \frac{P_1 V_2 - P_3 V_3}{\gamma - 1}. \quad (10)$$

Since

$$P_3 V_3^\gamma = P_1 V_2^\gamma, \quad (11)$$

and substituting into Equation 10 for  $P_3$ ,

$$\text{Energy (B to C)} = \frac{P_1 V_2 - P_1 (V_2/V_3)^\gamma V_3}{\gamma - 1}. \quad (12)$$

Since both numerator and denominator approach 0 as  $\gamma$  approaches 1, it is not clear what effect low values of  $\gamma$  will have on the energy. Thus, consider two expansion processes both beginning with the same initial pressure but having different  $\gamma$ 's,  $\gamma_f$  and  $\gamma_g$ , with  $\gamma_f > \gamma_g$ . Table 1 shows the energy ratios  $E_f/E_g$  (found from Equation 12) with three different expansion ratios  $V_3/V_2$ . The ratio  $E_f/E_g$  is less than 1, indicating that the process with the smaller  $\gamma$  imparts more energy to the projectile during the expansion process. As the gun barrel becomes longer (larger  $V_3/V_2$ ), the difference between the  $E$ 's becomes more pronounced. Thus, more energy is transferred to the projectile from the gases with the smaller  $\gamma$  during the expansion process.

To summarize, the propellant products with the smaller  $\gamma$  require more energy to attain a specified pressure during the constant pressure portion of the cycle, but some of this energy is recovered in the expansion process as the projectile moves down-bore.

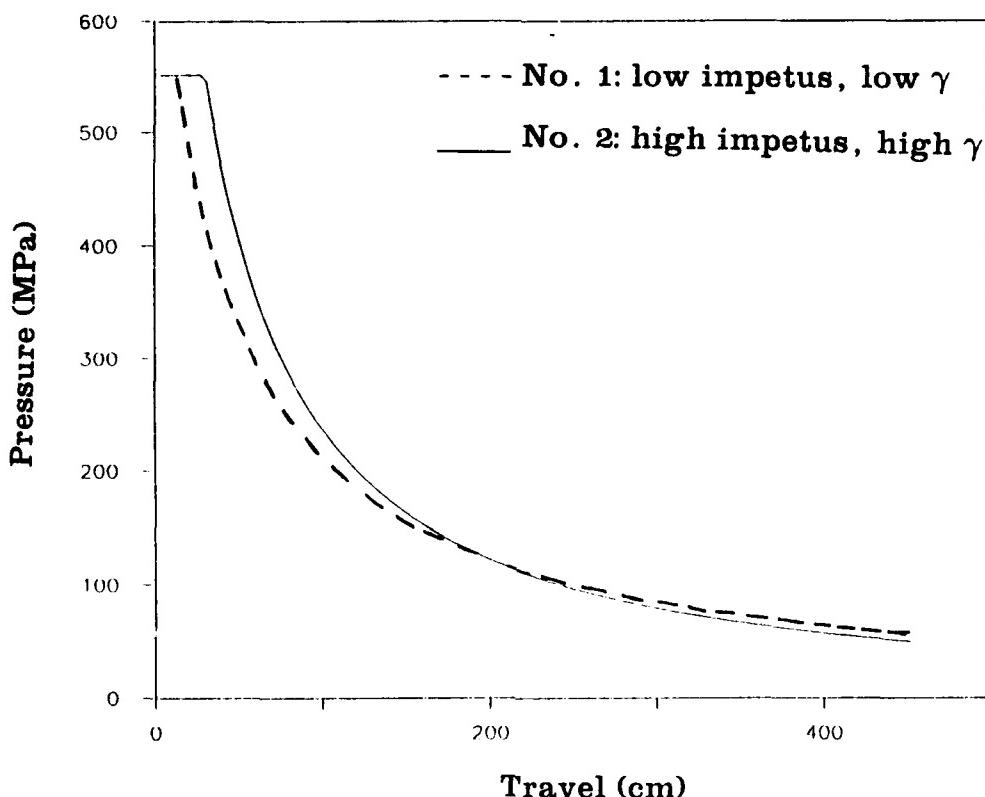
Table 1. Expansion Energy

| Energy Ratio<br>$E_f/E_g$ | Expansion Ratio<br>$V_3/V_2$ | Ratio of Specific Heats |            |
|---------------------------|------------------------------|-------------------------|------------|
|                           |                              | $\gamma_f$              | $\gamma_g$ |
| 0.79                      | 20:1                         | 1.25                    | 1.08       |
| 0.83                      | 10:1                         | 1.25                    | 1.08       |
| 0.87                      | 5:1                          | 1.25                    | 1.08       |

#### 4. PROPELLANT EVALUATION

As indicated in the previous section,  $\gamma$ , as well as impetus, must be considered in evaluating propellant performance. Two propellants were chosen to illustrate this fact: 1) a low impetus and a low  $\gamma$ , and 2) higher impetus and larger  $\gamma$ . Table 2 gives the propellant properties along with the results of a constant breech pressure gun calculation. The projectile base pressure vs. distance is given in Figure 2. Both calculations utilize the same mass of propellant.

As seen in Figure 2, propellant 1 burns out earlier. However, the down-bore pressure eventually exceeds that of propellant 2 during the expansion process. This can be interpreted as follows. The small  $\gamma$  results in a requirement for more energy to maintain the same pressure, as some of the energy is required for the internal degrees of freedom of the products. However, during the expansion process, a portion of this energy is recovered as the energy stored in the internal degrees of freedom is used during the assumed equilibrium process to contribute to a higher down-bore temperature and pressure than that for propellant 2. Propellant 2 has an impetus 19% higher than propellant 1 and, from impetus considerations alone, should give a velocity increase of 9% (i.e.,  $[1.19]^{1/2} = 1.09$ ). Table 2 shows only a 3% difference in velocity. The energy regained in the expansion process results in this smaller velocity difference than that which would be expected if only impetus values were considered. In conclusion, to evaluate propellants when there are solids in the combustion products, complete interior ballistic calculations are required. The area under the base pressure vs. projectile travel curve is the determining factor in projectile velocity.



**Figure 2. Projectile Base Pressure vs. Travel for Case 1 (low impetus, high  $\gamma$ ) and Case 2 (high impetus, low  $\gamma$ ).**

**Table 2. Propellant Properties and Constant Pressure Gun Calculations**

| Propellant                    | Case 1 | Case 2 |
|-------------------------------|--------|--------|
| Impetus, (J/g)                | 920    | 1,142  |
| $\gamma$                      | 1.08   | 1.2257 |
| $T_f$                         | 3,450  | 3,450  |
| Impetus/( $\gamma$ -1), (J/g) | 11,500 | 5,060  |
| Velocity, (m/sec)             | 1,412  | 1,460  |

## 5. THERMOCHEMICAL CALCULATIONS FOR SOLIDS

Thermochemical codes such as BLAKE (Freedman 1982) are used to calculate characteristics of gun propellants such as the impetus,  $\gamma$ , molecular weight, covolume, etc.

These values are then used in interior ballistic codes to predict gun performance. A very small amount of solid products is formed for conventional propellants. The thermochemical code assumes that solid products do not contribute to the pressure that accelerates the projectile. The solid products are assumed to occupy volume, and in that sense, they alter the pressure. The  $\gamma$  for the system is calculated by BLAKE for the gas phase products only. In the interior ballistic calculation, these particles are assumed to be evenly distributed from the breech to the projectile base; however, stored energy in the particles is assumed not to be returned to the gases except by thermal transfer. The mass of the particles contributes to the calculation of the propellant charge mass to projectile mass ratio  $C/M$  and thus to the pressure drop between the projectile base and the chamber as, for instance, when using the Lagrange gradient.

Suppose the solid particles move down-tube and remain in thermal equilibrium with the gas phase products. The energy stored in these particles will then contribute to the acceleration of the projectile by exchanging energy with the gas phase component. It would then be useful to have an effective  $\gamma$  for this mixture so that interior ballistic calculations could account for this effect.

To determine the heat capacities for solids, the equation

$$c_p - c_v = \frac{TV_o\alpha^2}{\beta}, \quad (13)$$

where

$T$  = temperature,

$V_o$  = molar volume,

$\alpha$  = coefficient of thermal expansion,

$\beta$  = coefficient of compressibility

must be used. However, many of these data are not available, especially under gun chamber conditions. An alternative approach is to calculate an effective  $\gamma$  by considering the energetics of the process. Consider the reaction



where in the products, C are particulates, and D is a gas.

Total Energy = solid phase energy + gas phase energy,

or,

$$\frac{Impetus}{\gamma' - 1} = \int_{T_0}^{T'} c_p dT + \frac{Impetus}{\gamma - 1}. \quad (15)$$

A BLAKE thermochemistry calculation provides the gas phase impetus,  $\gamma$  and  $T_f$ . The JANAF tables provide a value for  $c_p$  for the solid phase products. From the above equation, we can derive an effective  $\gamma'$ , which can be used in interior ballistic calculations.

## 6. EQUILIBRIUM BETWEEN SOLIDS AND GASES

Do particles moving down the tube remain in equilibrium with the gas? The formalism of the heat transfer of particles in a flowing gas is outlined in Cohen and Decker (1982). An assumption is made that radiation losses from the particles are negligible, and that the particle velocities are nearly the same as the gas (i.e., the particles flow down the gun tube).

$$\frac{dT}{dt} = \frac{6h'(T' - T)}{C_p D}$$
$$h' = \frac{Nu k'}{D} \quad (16)$$

The prime ('') parameters refer to the gas phase; the others refer to the solid phase.

$h'$  = heat transfer coefficient.

$Nu$  = Nusselt number, which equals 2 with the assumption that the particles have a low velocity relative to the gas.

$k'$  = conductivity of the gas.

$C$  = heat capacity of the particles.

$\rho$  = density of the particles.

$D$  = diameter of the particles.

The solution yields

$$t = - \frac{C_p D^2}{12k'} \ln \left[ \frac{(T' - T_2)}{(T' - T_1)} \right]. \quad (17)$$

This represents the time it takes for a particle at  $T_1$  in a gas at a lower temperature  $T'$  to go to a final temperature,  $T_2$ . This time should be as short as possible so that the energy from the particles can be transferred to the gas during the ballistic process. Hydrogen gas has a large conductivity, especially at high temperatures, and so will be chosen as the gas. For 10- $\mu\text{m}$  diameter particles of a solid material in  $H_2$ , the relaxation time is on the order of 100  $\mu\text{sec}$  under the assumption that  $(T' - T_2)/(T' - T_1)$  is approximately 0.4. Larger particles will have a substantially longer relaxation time, and any gas other than  $H_2$ , which has a very high conductivity, will also lengthen the time. Thus, considering that the expansion process for large caliber guns occurs in times of the order of milliseconds, the equilibrium assumption appears plausible if the particle size is 10  $\mu\text{m}$  or less. In reality, experimental measurements must be carried out to determine if the particles are indeed in equilibrium with the gas.

## 7. BALLISTIC IMPLICATIONS

It is interesting to determine the effect of  $\gamma$  on the ballistics for a series of hypothetical propellants all with the same impetus but with different  $\gamma$ 's. This situation could exist if solid particles were formed, but some did not remain in equilibrium with the gas during the expansion process. The calculated muzzle velocities are given in Table 3. As can be seen, there is a 3.9% velocity decrease when  $\gamma$  changes from 1.04 up to 1.24. It may also be seen that the ballistic efficiency (muzzle energy/chemical energy) is very low for the low  $\gamma$  propellant. At muzzle exit, there is a substantial amount of energy stored in the gases and solids. This is consistent with Figure 2 in which the muzzle pressure for the low  $\gamma$  propellant 1 is higher than for 2. Thus, a longer gun tube could be used to extract more energy from this propellant.

**Table 3. Theoretical Ballistic Performance for M-256, 120-mm Gun With Constant Impetus and Varying  $\gamma$**

| $\gamma$ | velocity<br>(m/sec) | Energy<br>(J/g) | Ballistic<br>Efficiency<br>(%) |
|----------|---------------------|-----------------|--------------------------------|
| 1.04     | 1,829               | 35,000          | 3.7                            |
| 1.08     | 1,816               | 17,530          | 7.3                            |
| 1.12     | 1,802               | 11,680          | 11                             |
| 1.16     | 1,788               | 8,760           | 14                             |
| 1.20     | 1,773               | 7,010           | 17                             |
| 1.24     | 1,757               | 5,840           | 21                             |

Impetus = 1,402 J/g

Expansion ratio = 5.6

Pmax = 480 MPa

Proj mass = 8.8 kg

Charge mass = 11.3 kg

## 8. CONCLUSIONS

- (1) For propellants which produce large amounts of solid particulates, impetus is not a good figure of merit. A detailed interior ballistic calculation with an effective  $\gamma$  is required.
- (2) Propellants with small  $\gamma$  require more energy to attain a given pressure than propellants with large  $\gamma$ . However, these propellants with the smaller  $\gamma$  return greater amounts of energy to the projectile during the expansion portion of the ballistic cycle, for sufficiently high expansion ratios.
- (3) An effective  $\gamma$  for gas/solid phase mixture can be estimated for use in interior ballistic codes.
- (4) Thermal equilibrium between solids and gases is plausible for the interior ballistic process if particle sizes are under 10  $\mu\text{m}$  and the gases, like  $H_2$ , have a high conductivity.

(5) Lower  $\gamma$  propellants have lower ballistic efficiencies than conventional propellants. This does not mean that they cannot achieve good ballistic performance, but they must have larger chemical energy densities to achieve this performance.

Finally, although not addressed in this paper, propellants with different  $\gamma$ 's have different interior ballistic characteristics which could have an effect on required gun tube strength, wear and erosion characteristics, and muzzle blast.

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